Report on the analysis of residues from steatite and ceramic vessels from the site of Belmont, Shetland

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Introduction

Absorbed residues from one ceramic vessel (SWV109 [C232] X1052) and three steatite vessels (BWU06 [C075] X256, BWU09 [C040] X825 and BWU09 [C075] X909) were extracted and analysed by gas chromatography-mass spectrometry (GC-MS). A soil sample was also taken from the interior of the ceramic vessel. Visible residues from a further 19 steatite vessels were also analysed along with visible residue from sherd BWU09 [C077] X909.

Bulk carbon (C) and nitrogen (N) stable isotope ratios were also measured for the visible residues.

Methods

Sample preparation

To avoid contamination all tools and glassware were triple washed with solvent, nitrile gloves were worn at all times and high-purity (HPLC grade) reagents were used for all processes. A method blank was also processed with each batch of samples to monitor any contamination introduced during sample preparation and analysis.

Absorbed residues from ceramic and steatite sherds

Samples of approximately 0.2 – 1.0 g were drilled from both surfaces of each sherd using an electric drill (*Dremel*) with a tungsten carbide bit. Both surfaces were sampled to identify contamination from the burial environment and/or post excavation handling. Contamination of this kind is generally present in similar concentrations on both surfaces of a sherd while residues of archaeological interest are usually present on only one surface. The samples from the ceramic sherd were drilled from two separate sherds near the base of the vessel – the interior from sherd 14 and the exterior from sherd 13 (see report from conservation for the exact position of the numbered sherds).

Each sample was accurately weighed. Extraction was carried out by sonicating the sherd powder with three aliquots of 5ml dichloromethane (DCM):methanol (2:1 v/v) for 15 minutes, followed by centrifugation for 10 minutes at 2000 rpm. Extracts were pipetted into clean vials and solvent removed by evaporation under a gentle stream of dry nitrogen combined with heating at 40°C. Prior to analysis by gas chromatography-mass spectrometry a measured amount of internal standard (C34 *n*-alkane) was added to each sample. The samples were then derivatised by heating at 70°C for two hours with an excess (approximately 50 µl) of bis(trimethylsilyl)trifuoroacetamide (BSTFA) with 1% trimethylchlorosilane (TMS). Excess BSTFA was removed by evaporation before analysis and the samples were re-dissolved in DCM for analysis.

Visible residues

Samples of these residues had been scraped off the sherds using a clean scalpel blade prior to arrival in the lab for analysis. Many of these were extremely abundant samples of 0.4 – 1.4 g taken from the material available using a clean spatula. These samples were ground to a powder using an agate pestle and mortar, accurately weighed into clean scintillation vials and extracted using the method above before analysis by GC-MS.

For bulk stable isotope analysis the samples were dried and weighed into tin capsules.

Soil sample from interior fill of ceramic sherd

The soil sample was taken from the surface of the fill of the vessel as revealed when the ceramic pieces were removed. This had been in contact with the interior surface of the vessel in the burial environment. A small amount (0.64 g) was removed with a scalpel, ground to a powder using an agate pestle and mortar and accurately weighed into a clean scintillation vial. Sample preparation was carried out as detailed above.

GC-MS analysis

GC-MS analysis was carried out on an Agilent 7890A series GC 5975C Inert XL mass selective detector. The splitless injector and interface were maintained at 300°C and 340°C, respectively. Helium was the carrier gas at constant inlet pressure. The column was inserted directly into the ion source of the mass spectrometer.The ionisation energy was 70eV and spectra were obtained by scanning between *m/z* 50 and 800. All samples were analysed using an Agilent DB5-ms-UI 15m x 2.5mm x 2.5 µm column. The oven temperature was programmed to be isothermal at 50°C for 2 minutes, followed by a rise of 10°C per minute up to 340°C and an isothermal hold for 10 minutes. Compounds were identified by comparison with the NIST library of mass spectral data and published data. Peak area measurements for quantification were carried out using the interactive RTE integrator within the Agilent Chemstation enhanced data analysis software. Abundances were calculated as µg of compound per gram of sherd.

Bulk stable isotope analysis

Carbon and nitrogen isotope analyses were performed on a Europa 20-20 mass spectrometer fitted with a Roboprep combustion unit. All samples were determined in duplicate and the results averaged.

Results and discussion

In general the residues were very well preserved with relatively little indication of modern contaminants. Phthalates were present in most samples but often at very low levels. These are usually the result of storing samples in plastic bags. Other contaminants will be discussed below. The ceramic sherd, two of the three steatite sherds and 12 of the 20 visible residues examined yielded residues of archaeological significance. The results are summarised in table 1.

Absorbed residues from sherds

Ceramic sherd SWU09 [C232] X1052 and associated soil sample

Figure 1 shows the total ion chromatograms produced by the interior and exterior residues extracted from the vessel and the soil. Both the interior and the exterior surfaces of this vessel yielded residues containing a series of odd, even and branched fatty acids ($C_{7:0}$ – $C_{31:0}$) dominated by $C_{16:0}$ (palmitic/hexadecanoic acid) and $C_{18:0}$ (stearic/octadecanoic acid)

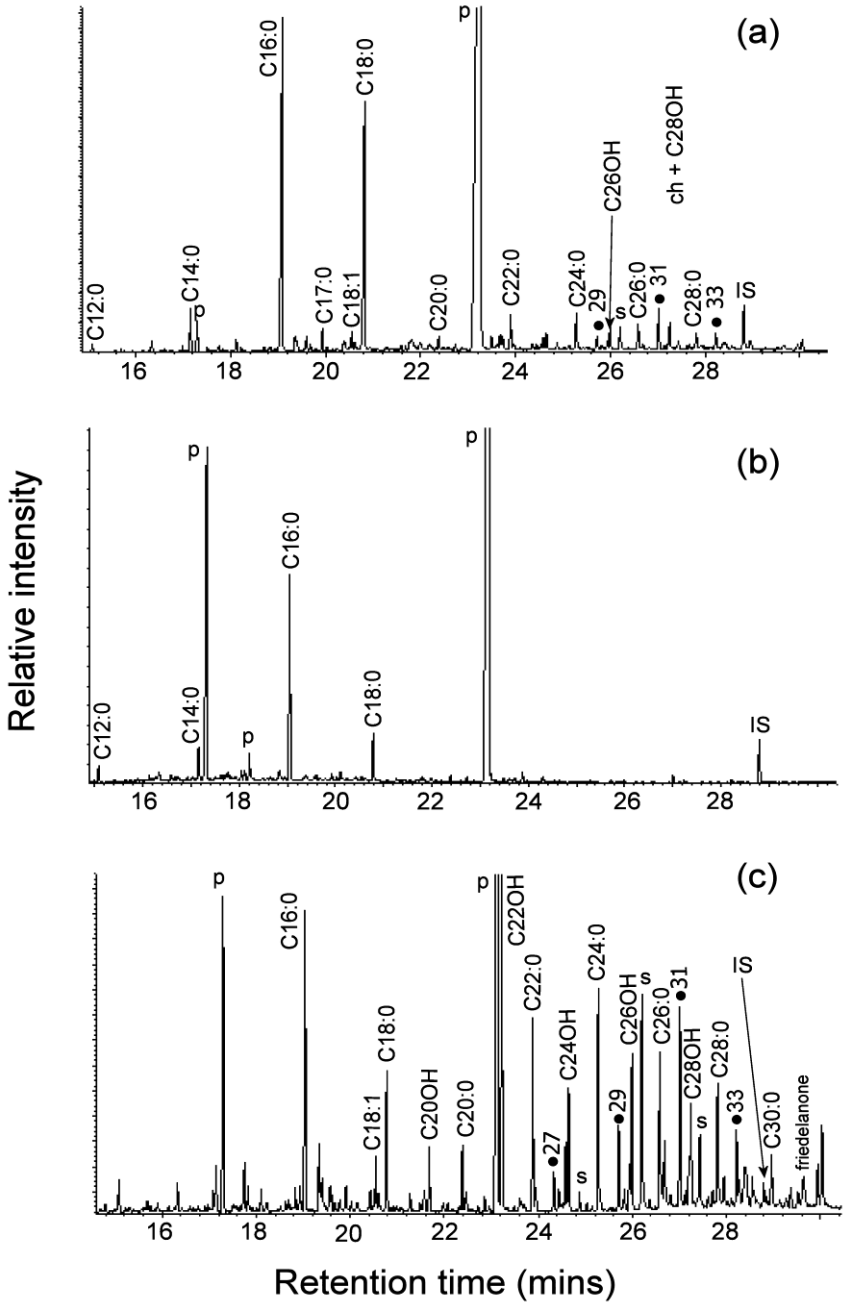

Figure 1: The chromatograms produced by the interior residue (a), exterior residue (b) and associated soil (c) from ceramic vessel C232 x1052. IS – internal standard, Cx:y – fatty acid with x carbons and y

which are biomarkers for degraded fats (Evershed, 1993, Heron and Evershed, 1993, Evershed, 2008a). The interior residue also contains low levels of long chain monounsaturated fatty acids ($C_{16:1}$ – $C_{24:1}$) and monoacylglycerols (C14, C16, C18) together with traces of the polyunsaturated fatty acid $C_{18:2}$, the two isoprenoid fatty acids 4,8,12-trimethyltridecanoic acid (TMTD) and phytanic acid (3,7,11,15-tetramethylhexadecanoic acid), hydroxy and dihydroxy fatty acids including 11,12-dihydroxydocosanoic acid, cholesterol and a series of cholesterol oxidation products. Trace components also include

long chain, even carbon numbered alcohols (C24 – C30), odd carbon numbered alkanes (C25 – C33), hexa- and octadecenamide, 2-hepta- and 2-nonacosanone and an homologous series of unidentified compounds eluting between 11 and 17 minutes. Most degraded fats consist mainly of $C_{16:0}$ and $C_{18:0}$ fatty acids regardless of their origin (Heron and Evershed, 1993, Stern *et al.*, 2000, Evershed, 2008a) and few fats contain distinctive biomarkers which allow a unique identification of the fat from biomolecular evidence alone. This particular residue does contain some $C_{17:0}$, both branched and straight chain, which might be indicative of a ruminant animal fat (Gunstone, 2004, 20-21). However the presence of two isoprenoid fatty acids together with long chain saturated and unsaturated fatty acids and the dihydroxy fatty acids, particularly 11,12-dihydroxydocosanoic acid, may indicate the presence of aquatic fats (Evershed, 2008b, Hansel and Evershed, 2009). However the other main biomarkers for aquatic fats, ω-(*o*-alkylpheny)alkanoic acids, are not present so no firm conclusions can be drawn from this (Hansel *et al.*, 2004, Craig *et al.*, 2007, Evershed, 2008b). The presence of mono-acylglycerols, produced by the partial degradation of the triacylglycerols which are the main components of fresh fats and oils (Gunstone, 2004, 23-32, Pollard and Heron, 2008, 150), indicates that this residue is relatively well preserved as these compounds readily degrade to yield free fatty acids and glycerol. The trace components may indicate the presence of plant material in the contents of the vessel but are more likely to represent the surrounding soil (see below).

The exterior residue also yielded saturated fatty acids ($C_{9:0}$ – $C_{24:0}$) and monounsaturated fatty acids ($C_{16:1}$ and $C_{22:1}$) although at lower abundances than the interior residue. Traces of phytanic acid and TMTD are also present along with the C16 and C18 monoacylglycerols. Traces of long chain, even carbon numbered alcohols (C24 – C28) and odd carbon numbered alkanes (C25 – C33) are also present. The exterior residue does not appear to be contamination from the surrounding soil (see below) as many of the compounds found in the soil sample are absent or present at very low abundances. This may represent spillage of the contents of the vessel.

The soil sample yielded a series of saturated fatty acids ($C_{8:0}$ – $C_{30:0}$), the monounsaturated fatty acids $C_{16:1}$ and $C_{18:1}$ and traces of monoacylglycerols (C15, C16). Significant abundances of even chain alcohols (C20 – C28), odd numbered alkanes (C25 – C33), traces of sugars and plant sterols are also present. Although a similar range of compounds is present in the two absorbed residues the relative abundances of the fatty acids and other compounds, in particular the alkanes and alcohols, is very different in the two cases. In the absorbed residues the fatty acids form the majority of the residues while in the soil the $C_{16:0}$ and $C_{18:0}$ are present at similar abundances to the main alcohols and alkanes. Therefore it is reasonable to assume that the absorbed residues from the vessel are of archaeological significance although some interaction may have taken place with the surrounding soil during burial.

Steatite sherds

Of the three steatite sherds examined (BWU06 [C075] X256, BWU09 [C040] X825 and BWU09 [C075] X909) BWU06 [C075] X256 and BWU [C040] X825 yielded residues of archaeological importance. The chromatograms from the interior and exterior surfaces of these two sherds are shown in figures 2 and 3.

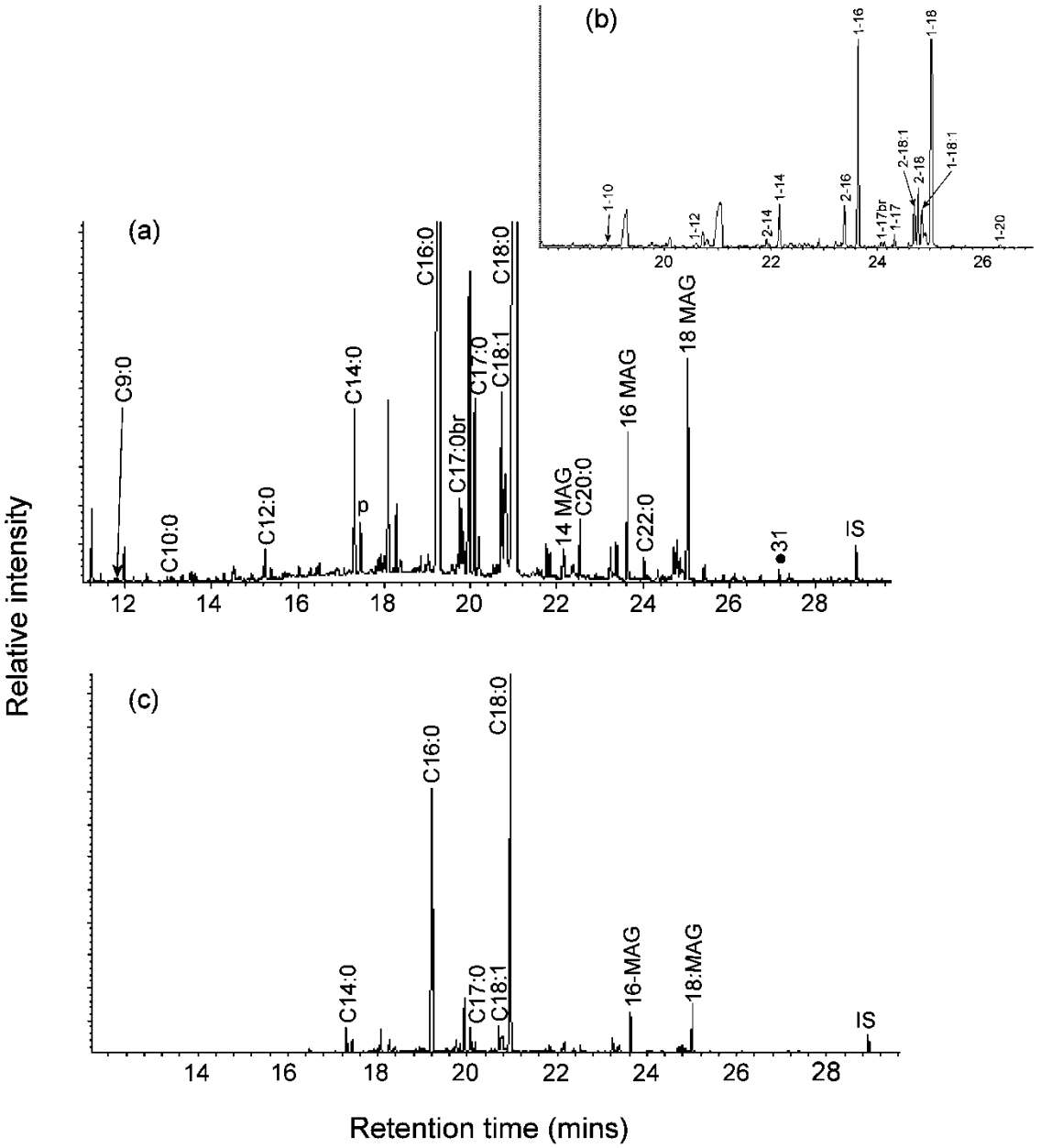

Figure 2: The absorbed residues from sherd BWU06 C075 x256 (a) total ion chromatogram produced by the interior residue; (b) the 147 ion extraction of the interior chromatogram showing monoacylglycerols; (c) the total ion chromatogram produced the exterior residue. IS – internal standard; Cx:y – fatty acid with x carbon atoms and y double bonds; br – branched isomer; x,y-MAG – monoaclylglycerol incorporating fatty acid with x carbon atoms at position y (assumed 1 if not present).

Both interior and exterior surfaces of BWU06 [C075] X256 show a range of odd, even and branched saturated fatty acids dominated by $C_{16:0}$ and $C_{18:0}$. Monounsaturated fatty acids ($C_{16:1}$ and $C_{18:1}$), a trace of the polyunsaturated $C_{18:2}$ acid and the isoprenoid phytanic acid are also present together with a range of both mono- (10-20) and diacylglycerols (32-36). The

presence of relatively abundant $C_{17:0}$ in both straight chain and branched form may indicate that this is a ruminant animal fat and a trace of cholesterol would support this view (Gunstone, 2004, 18-20). Short chain fatty acids ($C_{8:0}$ – $C_{12:0}$) and short chain monoacylglycerols down to C10 may indicate that milk was part of the original contents of the vessel (Evershed *et al.*, 2001, Gunstone, 2004, 18-20, 53). The identification of ketones (C31 and C33) shows that the fat has been cooked as they are a product of heating fats to high temperatures (Evershed *et al.*, 1995, Raven *et al.*, 1997). Traces of long chain alcohols with even numbers of carbon atoms (C20-C30), alkanes with odd numbered carbon atoms (C29-C33) and the plant sterol β-sitosterol may indicate the presence of plant material (Eglinton and Hamilton, 1967, Baker *et al.*, 1975, Bianchi, 1995) but may also come from soils (Heron *et al.*, 1991, Otto and Simpson, 2007). Although both interior and exterior surfaces yielded residues the interior residue is much more abundant than the exterior residue and can be interpreted as a residue of archaeological significance. The exterior residue is much less abundant than the interior but it is too abundant to be contamination and may represent spillage of the contents as it contains a similar range and distribution of compounds to the interior.

BWU09 [C040] X825 also contains a fatty residue on the interior surface although this is much less abundant than the residue in BWU06 [C075] X256. Saturated $C_{16:0}$ and $C_{18:0}$ fatty acids are only present at levels just above the minimum of 5 - 10 µg/g which is generally considered to represent background contamination (Stern *et al.*, 2000, Evershed, 2008b). Monoacylglycerols (14, 16, 18) were also present at levels greater than those of the free fatty acids, along with traces of the shorter chain monoacylglycerols (C8, C10, C12). This combination of compounds only allows the general identification of a degraded fat although the traces of short chain monoaclylglycerols suggest the presence of a dairy fat. The residue also contained significant amounts of phthalates from modern plastics and two isomers of 3-(4-methoxyphenyl)-2-propenoic acid, 2-ethylhexyl ester (octyl-4-methoxycinnamate) which is used in sun screens (Nakajima *et al.*, 2009). The residue from the exterior surface yielded a similar distribution of fatty acids, longer chain monoacylglycerols and octyl-4-methoxycinnamates, but at much lower concentrations with only the C16 monoacylglycerol, the two main phthalate peaks and one of the octyl-4-methoxycinnamate isomers above 5 µg/g. This exterior surface also yielded significant abundances of the saccharides glucose and mycose which are probably from the soil at the burial site (Simoneit *et al.*, 2004) and are not present on the interior surface. The presence of significant abundances of sun screen components may throw some doubt on the archaeological origin of this residue as sun screens may also contain fatty material.

Sherd BWU09 [C075] X909 contained no residues of archaeological significance. Low levels of fatty acids and monoacylglycerols were present but all at less 5 µg/g and at very similar levels in exterior and interior samples. Both interior and exterior residues also contain the poly-unsaturated hydrocarbon squalene and cholesterol. Cholesterol is indicative of animal fats (Gunstone, 2004, 21) and is present in human skin (Grenacher and Guerin, 1994). Squalene is also a component of human skin lipids (Goetz *et al.*, 1982, Grenacher and Guerin, 1994) but degrades rapidly because of its high degree of unsaturation and is unlikely to survive over archaeological time (Evershed, 1993). The presence of both compounds in residues is considered to indicate modern contamination from handling (Evershed, 1993). Both residues are also contaminated with siloxanes which probably formed as a biproduct of the derivatisation process during sample processing or represent contamination from

plastic vial lids or other plastic materials in contact with the sherd or the extracted sample (Chambers *et al.*, 2005). Both samples also contain traces of octyl-4-methoxycinnamate probably from sunscreen.

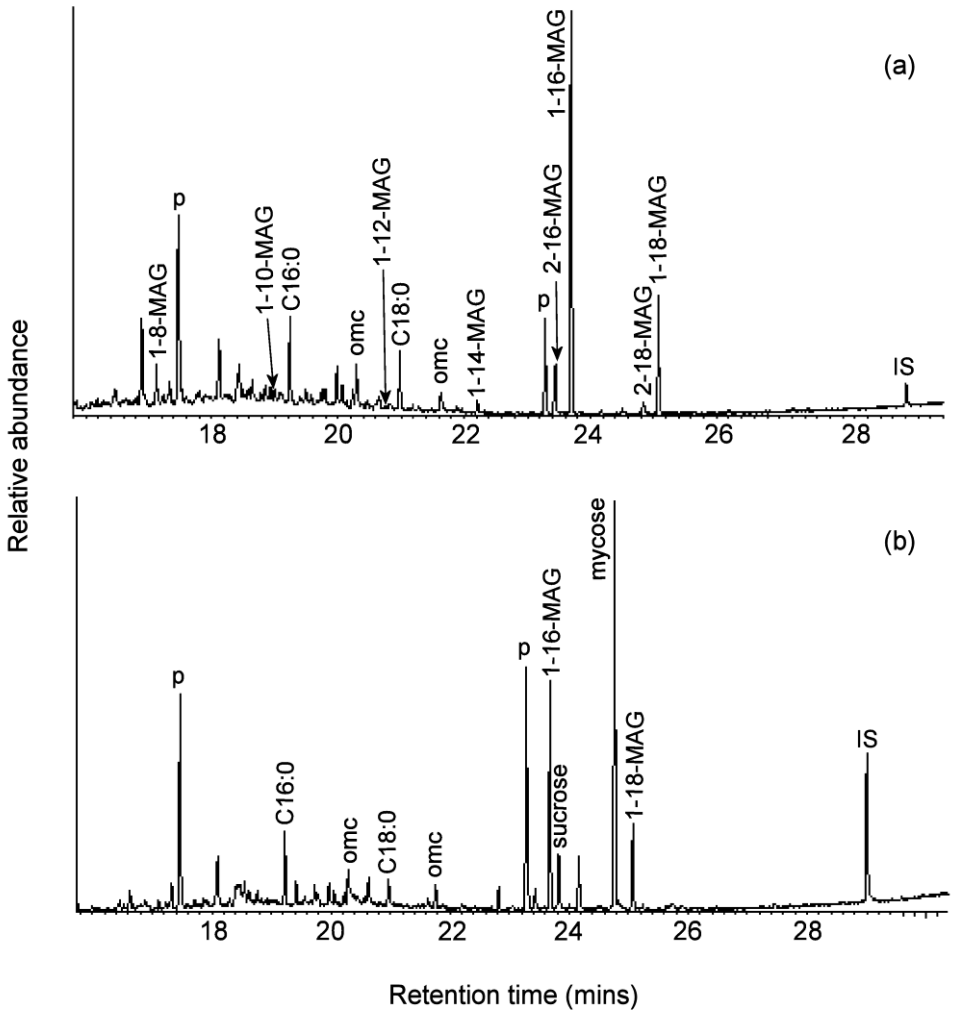

Figure 3: chromatograms produced by the interior (a) and exterior (b) residues extracted from sherd BWU09 C040 x825. IS – internal standard; p – phthalate; Cx:y – fatty acid with x carbon atoms and y double bonds; y-x-MAG – monoacylglycerol incorporating a fatty acid with x carbons at position y; omc – octyl-4-methoxycinnamate

Visible residues

The visible residues can be divided into four distinct groups:

- Residues which show evidence of cooked marine fats
- Residues with evidence of dairy fats
- Fatty residues with no distinguishing features

- The remaining residues containing little or no evidence of fatty material, sometimes with evidence of other materials

These residues are generally well preserved with only five out of the 20 samples showing no compounds of archaeological interest.

Residues containing marine fats

Of the 20 residues analysed, seven (BWU09 [C040] X826, [C167] X912, [C147] X981, [C167] X1004, [C167] X1040, [C075] X1113 and [C157] X1172) contain a range of biomarkers characteristic of aquatic fats, two further residues (BWU06 X184 and BWU09 [C147] X904) shows a high proportion of the same biomarkers and another (BWU09 [C021] X727) has some features which may indicate at least a proportion of marine fats in the residue. Figure 4 shows a typical example, BWU09 [C167] X912. These biomarker compounds include a range of saturated and in particular long chain (›$C_{18:0}$) fatty acids; a range of long chain monounsaturated fatty acids (›$C_{18:1}$); polyunsaturated fatty acids; the isoprenoid fatty acids 4,8,12-trimethyltridecanoic acid (TMTD) and phytanic acid (3,7,11,15-tetramethylhexadecanoic acid); hydroxy- and dihydroxy-fatty acids, in particular 11,12-dihydroxydodecanoic acid; and a range of ω-(*o*-alkylphenyl)alkanoic acids including C22 (Hansel *et al.*, 2004, Craig *et al.*, 2007, Evershed, 2008b, Hansel and Evershed, 2009). All biomarkers were present in three of the seven samples, while the remaining four lacked either dihydroxy- or polyunsaturated fatty acids. The presence of the ω-(*o*-alkylphenyl) fatty acids indicates that these aquatic fats were heated as they form by thermal degradation of the polyunsaturated long chain fatty acids which are common in aquatic tissue (Hansel *et al.*, 2004, Evershed, 2008b). BWU09 [C040] X826 and BWU09 [C147] X981 also contains a form of organic sulphur (S_8) which is normally associated with residues that have been buried in a waterlogged/underwater site.

BWU09 [C147] X904 does not show any evidence of ω-(*o*-alkylphenyl) acids but does contain all the other biomarkers for aquatic fats. BWU06 X184 contains a wide range of fatty acids up to $C_{28:0}$, a wide range of monounsaturated fatty acids ($C_{16:1}$ – $C_{24:1}$), TMTD and phytanic acid. However it only contains C18 and C20 ω-(*o*-alkylphenyl)alkanoic acids and C18 mono- and dihydroxy fatty acids.

BWU09 [C021] X727 contains only some of the biomarkers associated with aquatic fats. These include TMTD, phytanic acid, long chain monounsaturated fatty acids and the polyunsaturated $C_{18:2}$. No ω-(*o*-alkylphenyl)alkanoic acids are present although cholesterol and a range of cholesterol degradation products is present. Cholesterol is usually associated with animal fats but is also present in large amounts in some marine mammal oils (Stern, 2009) and in shellfish and eels (Holland *et al.*, 1993, 55, 75, 79, 83). The isotopic results support the identification of marine fat in this residue as it shares the highest $\delta^{13}C$ value (-23.5 ‰) and the second highest $\delta^{15}N$ value (11.6 ‰) (see below).

A plot of the bulk stable isotope values for nitrogen ($\delta^{15}N$) and carbon ($\delta^{13}C$) is shown in figure 5, and the values are shown in table 2. It is difficult to assess exactly what is being measured in a bulk carbon isotope analysis of archaeological residues as carbon may be present from more than one source – protein, fat, carbohydrates – and the exact contribution from each source is not known (Craig *et al.*, 2007). This means that the results

should be interpreted with a degree of caution. Foods from aquatic sources generally have higher $\delta^{15}N$ values than terrestrial foods due to the longer food chains in aquatic environments (Craig *et al.*, 2007). Fats from marine sources have higher $\delta^{13}C$ values (› -26 ‰), while those from freshwater sources are depleted in ^{13}C (Fischer and Heinemeier, 2003, Craig *et al.*, 2007). All the samples containing aquatic biomarkers show a range of $\delta^{15}N$ of 7.5 to 11.5 ‰ and $\delta^{13}C$ values between -26 ‰ and -23 ‰, and appear to form a group which is distinct from the more terrestrial residues with the exception of two outliers. These values are not inconsistent with the values for marine fats and so support the biomarker evidence. It should be noted however that the amount of nitrogen present in most of these samples is very low (1-9%) reducing the reliability of the $\delta^{15}N$ measurements.

From the evidence above it is reasonable to conclude that these vessels were used for processing marine fats/cooking marine foods rich in fat. These might include the blubber or

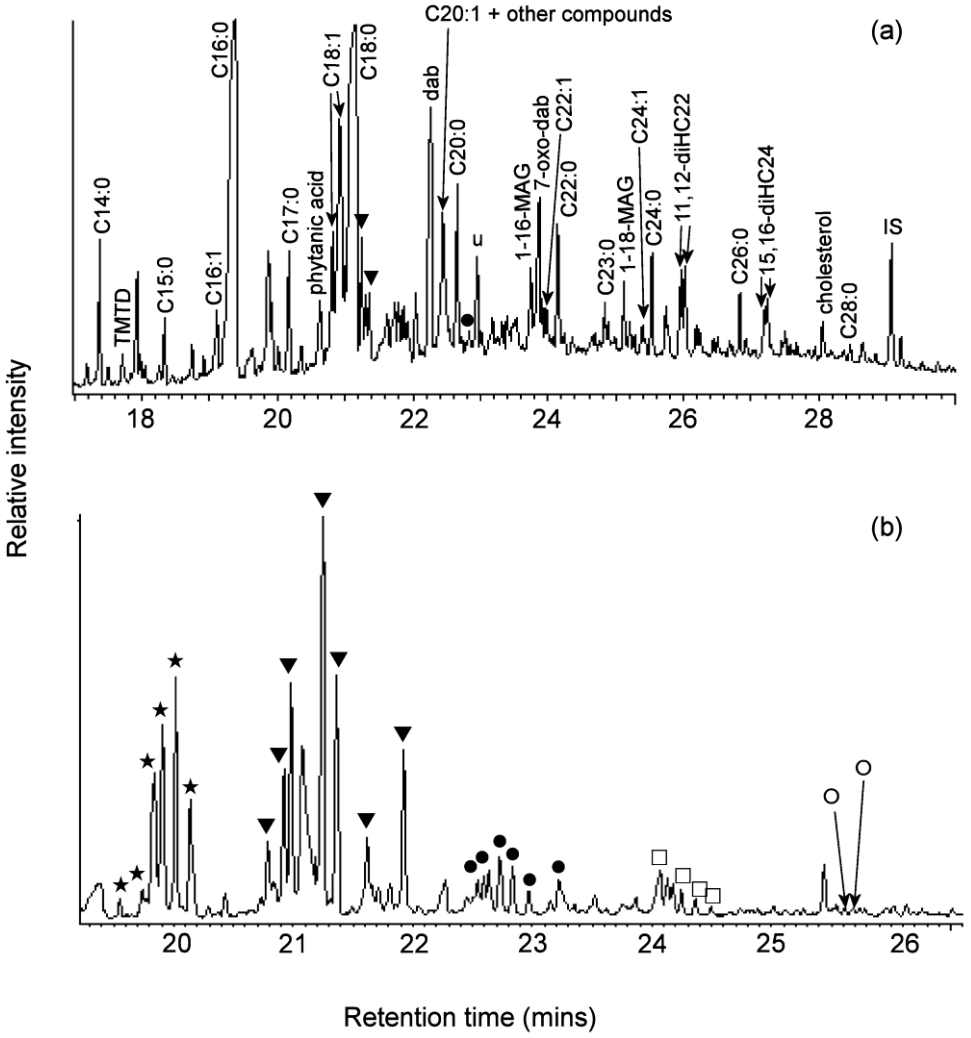

Figure 4: (a) total ion chromatogram produced by residue BWU09 C167 x912, (b) 105 ion extraction showing ω-(*o*-alkylphenyl)alkanoic acids. IS – internal standard; Cx:y – fatty acid with x carbon atoms and y double bonds; TMTD – 4,8,12-trimethyltridecanoic acid; x-y-MAG – monoacylglycerol incorporating a fatty acid with x carbon atoms at position y; a,b-diHCx – dihydroxy fatty acid with x carbon atoms, hydroxyl groups at positions a and b; dab – dehydroabietic acid; ★, ▼, ●, □, and O – ω-(*o*-alkylphenyl)alkanoic acids with 16, 18, 20, 22 and 24 carbon atoms respectively.

fat from marine mammals such as seals and whales, and fat/oil from eels or oily marine fish. White fish contains little in the way of fat and is unlikely to be the source material for these residues (Holland *et al.*, 1993). Other types of food may also have been cooked in these vessels as part of a mixed use (see below).

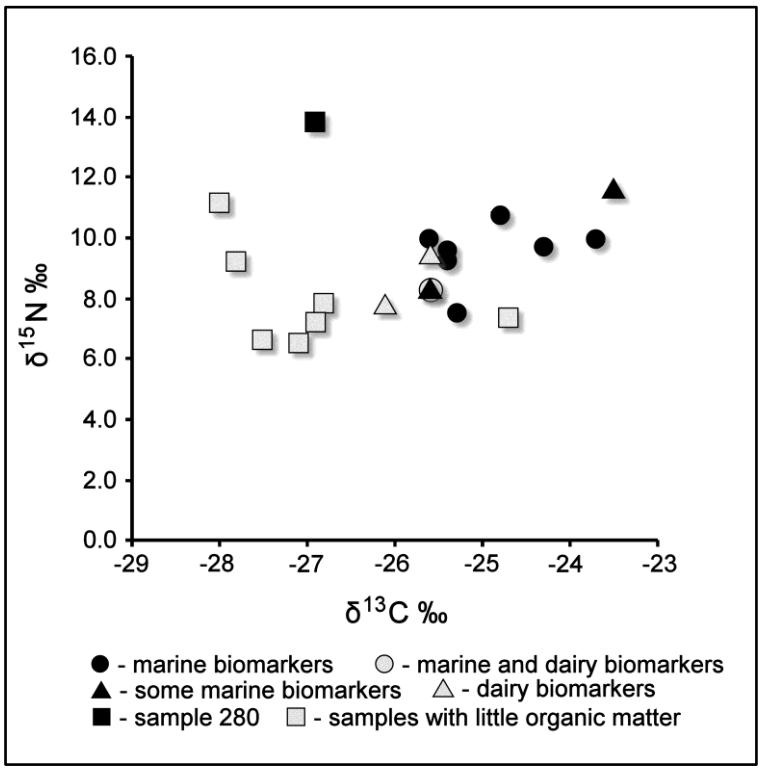

Figure 5: scatter plot showing the results of the bulk nitrogen and carbon stable isotope analysis

Residues showing evidence of dairy fats

Three residues (BWU06 [C075] X257, BWU09 [C075] X1095 and BWU09 [C040] X826) show evidence of dairy fats. They all contain short chain fatty acids down to $C_{8:0}$ and, in the case of BWU06 [C075] X257, down to $C_{6:0}$. Most of the residues in this study showed traces of short chain fatty acids so this alone cannot be taken as an indication of dairy fats. However BWU06 [C075] X257, BWU09 [C075] X1095 and BWU09 [C040] X826 also contain monoacylglycerols incorporating the fatty acids $C_{10:0}$ and $C_{12:0}$, while BWU09 [C075] X1095 and BWU09 [C040] X826 also shows the $C_{8:0}$ monoacylglcerol. It is interesting that BWU09 [C040] X826 also contains fish biomarkers indicating a mixture of materials were cooked/processed in this vessel. The bulk $\delta^{13}C$ value of this residue is -25.6 ‰ which is among the lowest of the marine-type residues and not inconsistent with a mixture of terrestrial and marine fats.

Without compound specific carbon isotopic analysis of the $C_{16:0}$ and $C_{18:0}$ fatty acids it is impossible to be certain that dairy fats are present but these three residues show features which would support this view.

Generic fatty residue with no distinguishing features

Two residues (BWU06 [C004] X280 and BWU09 [C185] X671) appear to contain a fatty residue with no distinguishing features. They show the range of odd, even and branched fatty acids dominated by $C_{16:0}$ and $C_{18:0}$ which is characteristic of degraded fats.

BWU06 [C004] X280 also contains traces of TMTD and phytanic acid together with C18 ω-(*o*-alkylpheny)alkanoic acids. Phytanic acid is present in plant material and C18 alkylphenyls form when plant material rich in monounsaturated $C_{18:1}$ is heated so these two biomarkers cannot be interpreted as the presence of aquatic fat (Hansel *et al.*, 2004). However TMTD is considered unique to aquatic environments (Craig *et al.*, 2007, Corr *et al.*, 2008). In addition the isotopic results could be consistent with at least a proportion of marine fat in this residue with $\delta^{15}N$ being the highest in the data set at 13.8 ‰. The $\delta^{13}C$ value by contrast is in the range for terrestrial fats at -26.9 ‰. This residue also contains a suite of compounds at lower abundances including long chain alcohols with an even over odd preference in carbon chain length (C16-C30, maximum at C22) and odd carbon chain numbered alkanes (C25-C33, maximum at C31) which are generally associated with plant material, along with dehydroabietic acid which is similarly associated with plants, conifers in particular (Mills and White, 1999, 99, Colombini *et al.*, 2000, Regert, 2004). These compounds can also be present in soils (Rogge *et al.*, 2007) and can also be found in the products of biomass burning (Simoneit, 2002). The residue also reveals compounds such as phenanthrene, fluoranthene, benzo(e)pyrene, ideno-pyrene, cyclo-ursanone, 2-heptacosanone, 2-nonacosanone, hopanes, oleanene, benz(a)anthracene and chrysene some of which may be present in soils but some of which are only present in wood tars or smoke from biomass burning (Hruza *et al.*, 1974, Simoneit, 2002, Rogge *et al.*, 2007). As this residue is from the exterior of the vessel the presence of compounds related to tars/smokes would not be unexpected.

For BWU09 [C185] X671 the isotopic results are within the range of terrestrial material. It also shows relatively high abundances of long chain, even carbon number alcohols (C20 – C30, maximum abundance C22) and also contains traces of sugars (figure 8). These compounds are generally associated with plant materials, in particular plant waxes (Eglinton and Hamilton, 1967, Baker *et al.*, 1975, Bianchi, 1995). However they can also be associated with soil lipids (Simoneit *et al.*, 2004, Rogge *et al.*, 2007) and are very similar in distribution to the lipids extracted from the soil sample associated with the ceramic vessel SWU09 [C232] X1052. However in BWU09 [C185] X671 the abundances of $C_{16:0}$ and $C_{18:0}$ are greater than would be expected from soil leading to the conclusion that this residue does contain fatty material from the use of the vessel in addition to compounds from the burial environment. Examination of the residue with a hand lens reveals the presence of fibres which may be related to the use of the vessel but may also be rootlets of plants. Further microscopic examination will be required to discover whether these fibres are part of the residue or the burial environment. If the site is, or has been, waterlogged these compounds may also have percolated into the residue from the surrounding soil (Jaffé *et al.*, 2006).

The remaining residues

The remaining six residues (BWU08 [C024] X532, BWU09 [C181] X788, BWU09 [C183] X811, BWU09 [C075] X909, BWU09 [C147] X991 and BWU09 [C147] X1093) either contain very little in the way of organic compounds or contain compounds which either represent plant material or contamination from the burial environment.

BWU08 [C024] X532, BWU09 [C181] X788, BWU09 [C183] X811 and BWU09 [C075] X909 contain very low levels of organic material which include fatty acids, long chain alcohols and alkanes. BWU09 [C147] X991 shows slightly higher abundances of $C_{16:0}$ fatty acid but is otherwise very similar to the other samples. BWU09 [C183] X811 and BWU09 [C075] X909 also contain traces of pimaric, isopimaric, dehydroabietic, abietic and 7-oxo-dehydroabietic acids which are generally associated with pine tar or resin (Mills and White, 1999, 99, Colombini *et al.*, 2000, Regert, 2004). However they can also be present in other plant material and have been detected in soil run-off and biomass smoke (Simoneit, 2002, Jaffé *et al.*, 2006). BWU08 [C024] X532, BWU09 [C147] X991 and BWU09 [C181] X788 also show low levels of compounds associated strongly with biomass smoke and/or soils including sugars, plant sterols and their oxidation products, 2-alkanones, phenols, friedelanone, vanillin, lupenones and hydroxycinnamic acid (Simoneit, 2002, Simoneit *et al.*, 2004, Jaffé *et al.*, 2006).

BWU09 [C147] X1093 shows relatively low abundances of $C_{16:0}$ and $C_{18:0}$ with higher abundances of long chain, even carbon numbered alcohols (C20-C30) with a maximum at C22 and traces of alkanes (C31, C33) together with long chain fatty acids ($C_{20:0}$ – $C_{32:0}$) and sugars. As discussed above this mixture of compounds may represent plant material but is more likely to be from soil lipids than from the contents of the vessel.

The isotopic results for this group of samples does not give any meaningful information as the residues appear to be composed mainly of plant material, soil lipids or biomass smoke. Apart from BWU09 [C147] X991 these samples contain almost no nitrogen (all ‹1%), making the $\delta^{15}N$ values unreliable. The nitrogen level in BWU09 [C147] X991 is still very low but is above 1%. This makes these samples the lowest in nitrogen content in this assemblage. These samples also have the lowest percentage of carbon in the assemblage. BWU09 [C181] X788 and BWU09 [C147] X1093 appear to contain fragments of rock or sand when examined with a hand lens and may be a mixture incorporating both the residue from the vessels and some sand or mineral particles from soil. More detailed examination with a microscope might identify what is going on in these residues.

Blanks

All blanks contain background levels of lipids (‹ 5 µg) with the exception of phthalates in the three of the five analysed. These are probably from the sample preparation or analysis and are modern materials unrelated to any archaeological residues.

Conclusions

In summary, the ceramic vessel [C232] X1052 contained a fatty residue which shows features of ruminant animal fat and also contains some of the biomarkers for aquatic fats. It is not possible to determine the exact nature of this fatty residue.

Of the three steatite sherds, two yielded interior residues. BWU06 [C075] X256 yielded an abundant residue from the interior surface which contains biomarkers associated with dairy fats and also contains compounds which form when fats are heated. The exterior surface yielded a similar residue at much lower abundances which may have been from spillage of

the vessel contents. BWU09 [C040] X825 also yielded small amounts of a fatty residue from the interior surface which may also have contained dairy. However the presence of sun screen ingredients as a significant proportion of this residue leads to a degree of doubt about the archaeological origins of the residue. BWU09 [C075] X909 did not contain any residues of archaeological significance and this is supported by the lack of organic compounds in the visible residue from the same sherd.

Nineteen further visible residues were analysed. Of these seven (BWU09 [C040] X826, [C167] X912, [C147] X981, [C167] X1004, [C167] X1040, [C075] X1113 and [C157] X1172) contain a range of biomarkers characteristic of aquatic fats and all but BWU09 [C040] X826 show bulk carbon and nitrogen isotope values which are not inconsistent with this interpretation. In addition BWU06 X184 and BWU09 [C147] X904 show many of the aquatic biomarkers and very similar isotopic values to the previous seven. BWU09 [C021] X727 also has some biomarkers which may indicate at least a proportion of aquatic fat in the residue and has a high $\delta^{15}N$ and high $\delta^{13}C$ values consistent with the presence of a marine fat as part of this residue.

Three residues (BWU06 [C075] X257, BWU09 [C075] X1095 and BWU09 [C040] X826) show biomarkers indicative of dairy fats. It should be noted that BWU09 [C040] X826 contained both aquatic and dairy biomarkers and the $\delta^{15}N$ and $\delta^{13}C$ values are at the lower end of the range for the marine fat samples and would not be inconsistent with a mixture of marine and dairy fats. This may be due to cooking dairy products and fish together or may represent separate uses of the vessel.

BWU06 [C004] X280 and BWU09 [C185] X671 contain fats of indeterminate origin. BWU06 [C004] X280 does contain a few biomarkers associated with aquatic fats and gave the highest $\delta^{15}N$ value in this assemblage. However more specific identification of the origin of the fatty material is not possible without compound specific stable isotope analysis. This sample also contains biomarkers consistent with biomass smoke/tar. As this is from the exterior of a vessel this is not a surprising discovery although it is not usually reported in archaeological material. BWU09 [C185] X671 is a fat but cannot be more specifically identified without further work.

The remaining five residues (BWU08 [C024] X532, BWU09 [C181] X788, BWU09 [C183] X811, BWU09 [C147] X991 and BWU09 [C147] X1093) contain no organic material of archaeological significance. BWU08 [C024] X532, BWU09 [C181] X788 and BWU09 [C183] X811 contain extremely low levels of organic compounds and could be highly carbonised residues formed by burning the contents of the vessels. BWU09 [C147] X991 and BWU09 [C147] X1093 show only a mixture of compounds which are common in humus rich soil and the smoke from burning biomass and must be considered to be either the remains of smoke deposition or contamination from the burial environment.

These results are highly significant as work on residues associated with stone vessels is still at the very early stages and only one paper has been published on the subject (Namdar *et al.*, 2009). Further work on the visible residues including compound specific stable isotope analysis to further characterise the sources of the fatty material in the residues would be a good extension of this work. Microscopic examination of the residues is also strongly recommended as this may assist in sorting out the source of plant-related compounds in the

residues. Phytolith and starch grain analysis might also prove useful in determining the origin of these plant related compounds.

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Sample	Saturated fatty acids	Unsaturated fatty acids	Isoprenoid fatty acids	ω-(*o*-alkylphenyl) alkanoic acids	Other lipids present
x1052:14i	$C_{7:0}$ – $C_{31:0}$	$C_{16:1}$ – $C_{24:1}$, $C_{18:2}$	TMTD, ph	nd	MAGs (14,16,18), mHFA (C18) and dHFAs (C20), 2-ketones (C17, C19), cholesterol, sugars, even alcohols (C20–C30), odd alkanes (C27–C33), p
x1052:13e	$C_{9:0}$ – $C_{24:0}$	$C_{16:1}$ – $C_{20:1}$	TMTD, ph	nd	tr odd alkanes (C25–C33), tr even alcohols (C24–C28), p
X1052 soil	Low levels $C_{16:0}$, $C_{18:0}$, tr $C_{8:0}$ – $C_{30:0}$	$C_{16:1}$ – $C_{18:1}$	tr TMTD, ph	nd	Odd alkanes (C27–C33), even alcohols (C20–C29), sugars, vanillin, friedooleanone, friedelanone, penatcosanone, stigmadienone, γ-elemene, p
BWU06 C075 x256i	$C_{8:0}$ – $C_{20:0}$	$C_{16:1}$ – $C_{18:1}$, $C_{18:2}$	ph	nd	MAGs (10–20), DAGs (30–36), dHFAs (C18), odd alkanes (C27–C33), alcohols e/o (C20–C29), tr sugars, cholesterol and oxidation products, β-sitosterol, ketones (C31, C33), tr p
BWU06 C075 x256e	$C_{12:0}$ – $C_{20:0}$	$C_{16:1}$, $C_{18:1}$	nd	nd	MAGs (10-20), DAGs (C30–C36), dHFAs (C18), tr alcohols, alkanes, sugars, cholesterol, tr p
BWU09 C040 x825i	$C_{14:0}$ – $C_{18:0}$	nd	nd	nd	MAGs (14-18), octyl-4-methoxycinnamate, p
BWU09 C040 x825e	tr $C_{14:0}$ – $C_{18:0}$	nd	nd	nd	MAGs (16, 18), sugars, octyl-4-methoxycinnamate, p
BWU09 C075 x909i	tr $C_{16:0}$, $C_{18:0}$	nd	nd	nd	tr MAGs (16,18), squalene, cholesterol, p, siloxanes
BWU09 C075 x909e	tr $C_{16:0}$, $C_{18:0}$	nd	nd	nd	tr MAGs (16,18), squalene, cholesterol, p, siloxanes
BWU09 C075 x909f	tr $C_{8:0}$ – $C_{24:0}$	tr $C_{16:1}$, $C_{18:1}$	nd	nd	tr MAGs (16,17,18), odd alkanes (C27–C33), tr even alcohols (C20–C28), isopimaric, abietic, dehydroabietic, unsaturated dehydroabietic acids, β-sitosterol, pristane
BWU06 x184f	$C_{6:0}$ – $C_{28:0}$	$C_{16:1}$ – $C_{24:1}$	tr TMTD, ph	C18, C20	MAGs (12–18), DAGs (28 – 34), mHFA (C18) and dHFAs (C18), cholesterol, β-sitosterol, tr sugars, p
BWU06 C075 x257f	$C_{6:0}$ – $C_{33:0}$	$C_{18:1}$, $C_{18:2}$	tr ph	nd	MAGs (10–18), DAGs (28–36), sugars, cholesterol and oxidation products, odd alkanes (C29–C33), tr e/o alcohols C23–C28), mHFA (C18), tr p

BWU06 C075 x280s	$C_{6:0}$ – $C_{28:0}$	tr $C_{16:1}$, $C_{18:1}$	tr ph	C18	tr MAGs (16,18), o/e alkanes (C25–C33), e/o alcohols (C22–C30), 2-ketones, friedelanone, lupenone, PAHs, hopanes related compounds including norhopane, p
BWU08 C024 x532f	$C_{7:0}$ – $C_{30:0}$	$C_{15:1}$ – $C_{19:1}$	tr ph	nd	MAGs (16), o/e alkanes (C23–C31), e/o alcohols (C20–C28), 2-ketones, β-sitosterol and oxidation products, friedelanone, lupenone, vanillin, jydroxycinnamic acid, sugars, γ-elemene, p
BWU09 C185 x671f	$C_{8:0}$ – $C_{28:0}$	$C_{16:1}$, $C_{18:1}$	nd	nd	MAGs (C16,C18), o/e alkanes (C23–C31), e/o alcohols (C21–C30), tr plant sterol, tr sugars, p
BWU09 C021 x727f	$C_{8:0}$ – $C_{22:0}$	$C_{16:1}$ – $C_{22:1}$, $C_{18:2}$	TMTD, ph	nd	MAGs (C18), cholesterol and oxidation products, β-sitosterol, sugars, friedelanone, PAHs, pimaric, isopimaric and dehydroabietic acids, p
BWU09 C181 x788f	tr $C_{16:0}$, $C_{18:0}$, $C_{24:0}$ – $C_{28:0}$	tr $C_{18:1}$	nd	nd	p, PAHs, sugars
BWU09 C183 x811f	tr $C_{14:0}$ – $C_{26:0}$	tr $C_{18:1}$	nd	nd	Low abundaces o/e alkanes (C21–C33), low abundances e/o (C18–C28), 2-ketones, dehydroabietic acid, PAHs
BWU09 C040 x826f	$C_{6:0}$ – $C_{30:0}$	$C_{16:1}$ – $C_{24:1}$, $C_{18:2}$	TMTD, ph	C16, C18, C20, tr C22	mHFA (C18), dHFA (C18), MAGs (8-18), DAGs (18-36), cholesterol and oxidation products, β-sitosterol, even alcohols (C22–C28), tr sugars, p, unsaturated dehydroabietic and 7-oxo-dehydroabietic acids, octyl-4-methoxycinnamate, p
BWU09 C147 x904f	$C_{7:0}$ – $C_{28:0}$	$C_{16:1}$ – $C_{24:1}$, $C_{18:2}$ – $C_{22:2}$	TMTD, ph	nd	Diacids (C4–C11), MAGs (C16,C18), dHFAs (C18,C20,C22), abundant cholesterol and oxidation products, abundant sugars, dehydroabietic, unsaturated dehydroabietic and, 7-oxo-dehydroabietic acids, tr p
BWU09 C167 x912f	$C_{7:0}$ – $C_{34:0}$	$C_{16:1}$ – $C_{22:1}$	TMTD, ph	C16, C18, C20, C22	MAGs (14–18), DAGs (30–36), mHFA (C18), dHFAs (C18,C20,C22), tr cholesterol, β-sitosterol, dehydroabietic acid, unsaturated dehydroabietic and 7-oxo-dehydroabietic acid, PAHs
BWU09 C147 x981f	$C_{8:0}$ – $C_{34:0}$	$C_{16:1}$ – $C_{22:1}$	TMTD, ph	C18, C20, C22	MAG (16), DAGs (32–34), dHFA (C22), alkanes (C31,C33), even alcohols (C22–C28), ketones, β-sitosterol, dehydroabietic acid, organic sulphur, tr p

BWU09 C147 x991f	low abundances $C_{8:0}$ – $C_{30:0}$	low abundances $C_{16:1}$, $C_{18:1}$	nd	nd	Low abundances MAGs (16,18), o/e alkanes (C25–C30), e/o alcohols (C20–C32), p, phytane, pristane, friedelanone, p,tr sugars
BWU09 C167 x1004f	$C_{8:0}$ – $C_{26:0}$	$C_{16:1}$ – $C_{22:1}$	TMTD, ph	C16, C18, C20, C22	Low abundances cholesterol, β-sitosterol, pimaric, unsaturated dehydroabietic and dehydroabietic acids, PAHs
BWU09 C075 x1040f	$C_{7;0}$ – $C_{34:0}$	$C_{18:1}$ – $C_{22:1}$	TMTD, ph	C18, C20, C22	Diacids (C4–C11), mHFAs (C20,C22), dHFAs (C18,C20,C22,C24), cholesterol and oxidation products, sugars
BWU09 C147 x1093f	$C_{8:0}$ – $C_{32:0}$, max $C_{22:0}$	$C_{16:1}$ – $C_{19:1}$	nd	nd	e/o alcohols (C20–C30), sugars, friedelanone, lupenone, β-sitosterol, hopane-like compounds,tr p
BWU09 C075 x1095f	$C_{8:0}$ – $C_{26:0}$	$C_{16:1}$, $C_{18:1}$	nd	nd	MAGs (8 – 18), tr cholesterol, β-sitosterol, campesterol
BWU09 C075 x1113f	$C_{9:0}$ – $C_{32:0}$	$C_{16:1}$ – $C_{24:1}$	TMTD, ph	C16, C18, C20, C22, C24	MAGs (14-18), DAGs (30–36), mHFA (C18), dHFA (C18), tr cholesterol, β-sitosterol, ketones (C31,C33), PAHs, sugars, p
BWU09 C157 x1172f	$C_{7:0}$ – $C_{32:0}$	$C_{18:1}$ – $C_{24:1}$	TMTD, ph	C16, C18, C20, C22	Diacids (C8,C9), dHFAs (C18,C20,C22), o/e ketones (C29–C34),

Key: i – interior absorbed residue; e – exterior absorbed residue; f – interior visible residue/foodcrust; s – exterior visible residue/sooted crust; $C_{x:y}$ – fatty acid with x carbon atoms and y double bonds; Cx – carbon chain of x carbon atoms; TMTD – 4,8,12-trimethyltridecanoic acid; ph – phytanic acid/3,7,11,15-tetramethylhexadecanoic acid; mHFA – monohydroxy fatty acid; dHFA – dihydroxy fatty acid; PAH – polyaromatic hydrocarbons; o/e – odd over even dominance; e/o – even over odd dominance; p – phthalate; tr – compound present at very low abundances

Table 1: summary of the biomolecular results

Sample	$\delta^{13}C$ (‰)	% C	$\delta^{15}N$ (‰)	% N
BWU06 x184f	-25.6	20.5	9.9	2.1
BWU06 C075 x257f	-26.1	7.7	7.8	7.9
BWU06 C075 x280s	-26.9	21.7	13.8	2.4
BWU08 C024 x532f	-27.1	9.2	6.5	0.6
BWU09 C185 x671f	-27.5	12.2	6.6	0.7
BWU09 C021 x727f	-23.5	26.9	11.8	1.7
BWU09 C181 x788f	-26.9	7.7	7.2	0.4
BWU09 C183 x811f	-26.8	8.0	7.8	0.6
BWU09 C040 x826f	-25.6	20.5	8.3	2.1
BWU09 C147 x904f	-25.3	47.6	7.5	1.5
BWU09 C075 x909	-24.7	47.6	7.3	0.3
BWU09 C167 x912f	-25.6	26.3	9.9	2.6
BWU09 C147 x981f	-24.3	28.4	9.7	1.2
BWU09 C147 x991f	-27.8	15.6	9.2	1.2
BWU09 C167 x1004f	-25.4	45.5	9.5	4.2
BWU09 C075 x1040f	-24.1	39.1	9.3	30.2
BWU09 C147 x1093f	-28.0	13.1	11.1	0.9
BWU09 C075 x1095f	-25.6	29.5	9.5	2.2
BWU09 C075 x1113f	-23.7	37.6	9.9	5.0
BWU09 C157 x1172f	-24.8	30.6	10.8	1.2

Key: f – interior visible residue/foodcrust; s – exterior visible residue/sooted crust

Table 2: Summary of the nitrogen and carbon bulk stable isotope analysis. NB Samples with a low % of nitrogen by weight (< 2 %) may not give reliable $\delta^{15}N$ values and have been shaded.